Oxygen-18 variations in Sulfate from living marine organisms

by

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After the development of oxygen-isotope temperature scales based on the measurement of the oxygen-18 content of carbonate [1] and phosphate [2] from shells of living marine organisms, the sulfate is the major remaining anion to be studied for paleoecologic research. A precise analytical method for the measurement of the oxygen isotopic composition of sulfates was developed in 1967 [3] based on the reduction of $BaSO_4$ with graphite at about 1100° C, and this technique was successfully applied in the last few years mainly in the case of dissolved sulfate in sea water and fresh water [4,5,6,7,8].

The purpose of this research was to try to establish a relationship between the growth temperature and the oxygen isotopic composition of the sulfate of living shells. The main difficulty in measuring the isotopic composition of such a sulfate was its separation and purification. The amount of sulfate ion present in the calcitic shells studied ranges from traces to about 0.3 per cent : no investigations have as yet been made on the crystal chemistry of the sulfate. If the powdered shells are dissolved in hydrochloric acid there exists the possibility of an isotopic exchange between the (SO_4^{2-}) ions, water and the CO_2 evolved. Acid treatment was then avoided and a partial separation of the sulfate was obtained by direct solution in bidistilled water. The shells were mechanically cleaned, then washed and air dried, crushed in a steel mortar and ground very finely in an agate mortar. The powder was suspended in bidistilled water and the suspension was stirred for 24 hours by means of a magnetic stirrer. The solution was filtered and

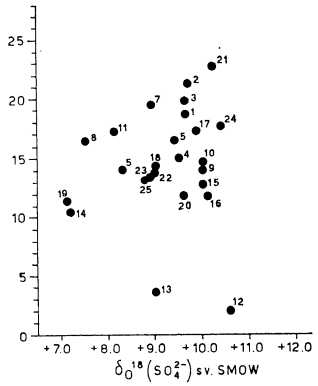

FIG. 1. — Oxygen isotopic composition of the sulfate in the species studied versus their average growth temperature as calculated from the $\delta 0^{18}(CO_3^{2-})$.

then passed through an ion exchange column packed with hydrous zirconium oxide. The sulfate was then precipitated from the eluate as $BaSO_4$ [5]. Naturally only a portion of the soluble sulfate which is present in the shell is measured using this technique. However we assume that the technique is valid and the results are correct because measurements carried out on the total sulfate separated by acid solution of the shells yielded equal or very similar values. Tests carried out on shells of different species using both the acid treatment and the simple solution in bidistilled water showed that the results are generally very close to one another but the δs obtained from acid treatment are generally slightly more negative

Rapp. Comm. int. Mer Médit., **21**, 7, pp. 355-357, 1fig. (1973).

the difference being 0.1 to 1.0 per mille. The difference is ascribed to isotopic exchange taking place between (SO_4^{2-}) ions and water under acid conditions. Further tests using enriched water are planned to clear up the matter completely.

The first group of measurements was carried out on Pelecypods from the Tyrrhenian Sea, then measurements were extended to shells collected in different areas for the purpose of studying organisms which were grown at different temperatures. In fact we expected to study organisms within a temperature range of some 25 °C.

The species studied, their location and the results obtained are given in Table 1. The standard deviation of the isotopic measurements (σ) is about $\pm$ 0.1 per mille. The values of $\delta 0^{18}(SO_4^{2-})$ are shown graphically in Fig. 1 against the average growth temperature of each species as calculated from the $\delta 0^{18}(CO_3^{2-})$. The isotopic results obtained are corrected for the isotopic effect of the environmental water. The values used for this correction are only approximate, however they have been deduced from measurements carried out directly on water samples from the different areas comparing the results obtained with similar data published by a number of authors.

The following conclusions can be drawn :

a. the range of the oxygen isotopic composition of the sulfate in the shells of Pelecypods and other marine organisms is about four per mille;

b. the average value of the samples measured is equal to the average value of the isotopic composition of the dissolved sea water sulfate;

c. there does not seem to exist any relationship between the average growth temperatures of the shells and their $\delta 0^{18}(SO_4^{2-})$;

d. the isotopic composition of the sulfate in the shells does not seem to be related to any conceivable variable like e.g. $\delta 0^{18}(H_2O)$, concentration of (SO_4^{2-}) in the shells etc.

From the above considerations one should conclude that, very likely, the sulfate in the shells is not involved in methabolic processes since such processes probably determine fractionation factors consistent with growth temperature or with other variables. In the case of the species studied the fractionation factors seem to be distributed at random and to depend more upon either the structural characters of the shells or some peculiar process of selection in the adsorption of sea water sulfate.

Under these circumstances it does not seem possible to obtain an isotopic temperature scale in the case of marine shell sulfate.

References

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TABLE 1 — Species studied, their location and isotopic results obtained.

N. of sample	Species	Location	Depth	$\delta^{18}(SO_4^{2-})$ ys. SMOW	$\delta^{18}(CO_3^{2-})$ ys.PDB-1	t° C from $\delta^{18}(CO_3^{2-})$	$\delta^{18}(H_2O)$ ys. SMOW
1	*Donax trunculus*	43°37'N 10°17'E	1	+ 10.6	+ 0.50	18.7	+ 1.0
2	*Venus gallina*	43°37'N 10°17'E	1	+ 10.7	— 0.11	21.4	+ 1.0
3	*Mactra corallina*	43°37'N 10°17'E	1	+ 10.6	+ 0.20	19.9	+ 1.0
4	*Solen marginatus*	43°37'N 10°17'E	1	+ 10.5	+ 1.40	15.0	+ 1.0
5	*Pinna nobilis*	Elba Isl.	5	+ 10.4	+ 1.00	16.5	+ 1.0
6	*Patella coerulea*	Genova	1	+ 9.3	+ 1.60	14.0	+ 1.0
7	*Mytilus galloprovincialis*	43°37'N 10°17'E	2	+ 9.9	+ 0.30	19.5	+ 1.0
8	*Sepia officinalis*	Tyrrhenian Sea		+ 8.5	+ 1.02	16.5	+ 1.0
9	*Cardium tuberculatum*	43°37'N 10°17'E	2	+ 11.0	+ 1.55	14.1	+ 1.0
10	*Solenocurtus strigilatus*	43°37'N 10°17'E	2	+ 11.0	+ 1.43	14.7	+ 1.0
11	*Mytilus californicus*	La Jolla, Calif.	1	+ 7.8	— 0.50	17.3	— 0.3
12	*Spisula solidissima*	44°11'N 49°25'W	50	+ 9.6	+ 2.87	2.0	— 1.0
13	*Chlamys islandica*	45°02'N 51°33'W	80	+ 8.0	+ 2.33	3.7	— 1.0
14	*Pecten novaezelandiae*	Stewart Isl. N.Z.	50	+ 7.1	+ 1.36	10.6	— 0.1
15	*Spisula aequilateralis*	41°00'S 174°55'E	2	+ 10.0	+ 0.92	12.7	0.0
16	*Mactra discors*	41°00'S 174°55'E	2	+ 10.1	+ 1.13	11.9	0.0
17	*Dosinia anus*	41°00'S 174°55'E	2	+ 9.8	— 0.20	17.3	0.0
18	*Mytilus planulatus*	Wellington N.Z.	2	+ 8.9	+ 0.42	14.3	— 0.1
19	*Neothyris lenticularis*	Stewart Isl. N.Z.	50	+ 7.0	+ 1.16	11.3	— 0.1
20	*Cookia sulcata*	Wellington N.Z.	2	+ 9.5	+ 1.04	11.8	— 0.1
21	*Tridacna elongata*	Bora-Bora	2	+ 10.4	— 1.18	22.8	+ 0.2
22	*Hinnites giganteum*	La Jolla, Calif.	20	+ 8.7	+ 0.29	13.9	— 0.3
23	*Hinnites giganteum*	La Jolla, Calif.	20	+ 8.6	+ 0.40	13.5	— 0.3
24	*Amiantis callosa*	La Jolla, Calif.	2	+ 10.1	— 0.59	17.8	— 0.3
25	*Haliotis rufescens*	La Jolla, Calif.	20	+ 8.5	+ 0.50	13.0	— 0.3